POTENTIALS OF IRON, 18-8 AND TITANIUM IN PASSIVATING SOLUTIONS

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ABSTRACT

Potentials of iron in chromates follow the Langmuir Adsorption Isotherm, as shown by the linear relation between $\frac{C}{\Delta E}$ vs C, where C is concentration and ΔE is change of potential. Maximum potential change corresponding to an adsorbed monolayer of chromate ions occurs at 0.0025 molar K_2CrO_4, which approximates the minimum concentration for passivity reported by Robertson. The evidence agrees with a primary mechanism of passivity based on adsorption rather than oxide film formation, especially since potentials of iron in several organic inhibitors, which are conceded to function by adsorption, also follow the adsorption isotherm as shown by Hackerman et al. Passivity of 18-8 stainless steel and titanium in sulfuric acid containing cupric or ferric salts appears similarly to be accompanied by adsorption of Cu^{++} or Fe^{+++}. The irreversible nature of the potentials is in accord with the view that the adsorbate, in part, is chemisorbed.

Hydroxyl ions in 4% NaCl produce more active potentials in passive 18-8 or titanium presumably by displacing adsorbed oxygen. Potentials of 18-8 in alkaline NaCl as a function of partial pressure of oxygen follow the adsorption isotherm, which adds confirming evidence that an adsorbed oxygen film is responsible for passivity. The decreased potentials between active and passive areas plus precipitation of passivity-destroying metal chlorides at

incipient anodes accounts for inhib ion of pitting in chloride solutions by alkalies.

Calculated Langmuir isotherm constants, taking into account competitive chemisorption processes, agree qualitat vely with expected relative values based on chemical properties of metals and adsorbates.

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Chromates are in the class of inhibitors called passivators because the potential of iron immersed in a chromate solution is several tenths volt more noble than in water, and iron no longer corrodes visibly. Two points of view have been proposed regarding the mechanism of passivation by these and similar compounds. Hoar and Evans[1] proposed that chromates react with soluble ferrous

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[1] T. P. Hoar and U. R. Evans, J. Chem. Soc., 1932, 2476

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salts throwing down a protective film of hydrated ferric and chromic oxides. Accordingly, a film of ferric oxide on air-exposed iron will, if introduced into chromates, be made more protective because the chromate "repairs" the film discontinuities. Since then, this view has been re-stated by several investigators[2,3,4]. Mayne and Pryor[3] modified the picture somewhat, based on their

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[2] T. P. Hoar, Trans. Faraday Soc., 45, 683 (1949).

[3] J. Mayne and M. Pryor, J. Chem. Soc., 1949, 1831

[4] M. J. Pryor and M. Cohen, J. Electrochem. Soc., 100, 203 (1953).

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electron diffraction studies, proposing initial adsorption of chromates followed by direct reaction with iron to form an unhydrated γ Fe$_2$O$_3$ film which they

suggested was a better diffusion barrier layer than a film of hydrated oxides.

A second view attributes passivity to adsorption of chromate ions on the metal surface[5,6,7,8]. Formation of an oxide film is considered unnecessary,

[5] H. H. Uhlig, Chem. Eng. News, 24, 3154 (1946).

[6] H. H. Uhlig, Metaux et Corrosion, 22, 204 (1947).

[7] "Corrosion Handbook", p. 31, edited by H. H. Uhlig, John Wiley & Sons, Inc., 1948.

[8] W. D. Robertson, J. Electrochem. Soc., 98, 94 (1951).

although such a film may form eventually and aid in the overall protection. The primary protection, however, is considered to result from satisfaction of valence forces of the surface metal atoms by chemical bonding with chromate ions, and without the metal atoms leaving their respective lattices. A similar mechanism has been proposed for specific organic inhibitors[9].

[9] N. Hackerman and H. Schmidt, Corrosion, 5, 237 (1949).

Passivators, in accord with this view, are substances having high affinity for the metal, and accompanying high activation energy for any reaction which results in a new lattice belonging to a surface stoichiometric compound. These are the essential conditions for chemisorption. Consequently, an iron-chromium oxide or iron oxide, whichever forms ultimately when iron is exposed to chromate solutions, accumulates only slowly. Chlorine, for example, is not a passivator because, despite high affinity for the metal, its activation energy for reaction is low, resulting in rapid production of iron chlorides rather than a chemisorbed

film of chlorine atoms. Oxygen, by way of contrast, readily chemisorbs on many metals and is a good passivator. Halide ions break down passivity by competing with oxygen or other passivators for a place on the metal surface; but once they succeed, metal corrodes at such areas until additional passivator adsorbs.

Evans[10] and others[1,3,11] isolated oxide films on iron exposed to

[10] U. R. Evans, J. Chem. Soc., 1927, 1020

[11] U. R. Evans and J. Stockdale, J. Chem. Soc., 1929, 2651

chromates and supposed these to be the primary source of protection. Circumstantial evidence of this kind is not conclusive, however, in view of the primary process of adsorption which, if it occurs at all, always precedes the formation of oxides or other compounds, and continues in effect even after the usually permeable, although relatively thick oxide films are formed. In specific instances, some chemical reagents used for stripping of surface films may actually produce an oxide reaction product[12,13]. When this is the case, the stripping

[12] W. Vernon, F. Wormwell and T. Nurse, J. Iron and Steel Inst. (London) 150, 81P (1944).

[13] M. Fontana, Discussion Section Trans. Electrochem. Soc., 93, 335 (1948).

reagent may hasten reaction of adsorbed films, if not of other substances, with the metal, resulting in a surface compound where none existed before.

McKinney and Warner[14] in discussing a paper by Evans expressed doubt

[14] D. McKinney and J. C. Warner, Ind. and Eng. Chem., 37, 705 (1945).

that chromates could act merely by precipitation of ferric-chromic oxides on the metal surface, in view of the fact that chromic salts are relatively poor inhibitors compared with chromates. Evans[15] replied that when chromic salts pre-

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[15] U. R. Evans, Ibid, p. 706.

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cipitate a film of hydrated chromic oxide on cathodic areas, attack is not hindered; whereas with chromates mixed hydroxides are precipitated locally at places where anodic attack would otherwise set in and prevents it from developing. This explanation, however, is less convincing in light of Robertson's[8] subsequent data which showed that molybdates and tungstates, analogous to chromates structurally, and inhibiting at the same minimum concentration, fail to oxidize ferrous salts, (or do so extremely slowly[4]) and, hence, are quite unlike chromates in their capacity to precipitate a supposed protective anodic coating*.

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*Criticism of Robertson's conclusions has been made on the basis that the otherwise weak oxidizing capacity of molybdate and tungstate in acid solution might be greater in neutral solutions[16] corresponding to conditions of pH at the surface

[16] M. Pryor and M. Cohen, Discussion Section, J. Electrochem. Soc., 98, 513 (1951).

of iron. However, the oxidizing tendency of these salts is less in neutral or alkaline media as compared with acid solutions, (as can be demonstrated thermodynamically) and, hence, if oxidation does not proceed in acid media it is certainly not expected under conditions of higher pH. This in fact was demonstrated for molybdates and tungstates by Pryor and Cohen through titrations in neutral media. They found only 11% of 0.0072 N ferrous sulfate to be oxidized by 0.1 N sodium tungstate after as long a period as three days, although they interpret this slow rate as sufficient to form the supposed protective film. Actually, molybdates and tungstates are less effective oxidizers than is dissolved oxygen.

This is not to say that iron does not reduce molybdates and tungstates in solution and become oxidized in the process. However, the minimum concentration of these substances for passivity or inhibition, identical with the minimum concentration of chromates despite differing oxidizing tendencies compared with chromates or with dissolved oxygen, suggests a mechanism of protection dependent on something other than an oxidation reaction leading to impermeable oxide film formation.

Rozenfel'd and Akimov leaned to the possibility that anodic polarization of iron by chromates was due to adsorption of the chromate ion[17]. Indelli[18]

[17] I. Rozenfel'd and G. Akimov, Doklady Akad. Nauk. S.S.S.R., 67, 379 (1949); Chem. Abst., 44, 459 (1950).

[18] A. Indelli, Ann. Chim. (Rome) 40, 189 (1950); Chem. Abst., 45, 10177 (1951).

also interpreted potential behavior of iron and 18-8 in chromates in terms of adsorption of the inhibiting ion.

Simnad[19] using radioactive chromium concluded that the view of Hoar and

[19] M. Simnad, J. Inst. Metals Monograph No. 13, p. 23, London (1953).

Evans was corroborated by the almost similar pick-up of radioactive chromium whether iron was immersed in chromic chloride or in chromates, and by the spotty deposition of radio-chromium salts on an iron surface exposed to chromates, presumably revealing anode areas. However, his conclusions do not take into account reaction of chromic chloride with iron to form hydrated oxides which adhere to the metal surface in the same manner as hydrous Fe_2O, but which are not protective in the same sense as chromates. Similarly, chromates may be reduced at preferential metal areas, particularly if chlorides or sulfates in solution are present which accelerate consumption of the passivator[20].

[20] M. Darrin, Ind. Eng. Chem., 38, 363 (1946).

Impurities in the metal may also accelerate reduction of chromates.

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Brasher and Stove[21] based on similar studies using radioactive chromium

[21] D. Brasher and E. Stove, Chem. and Ind., No. 8, 171 (1952).

as chromate report that the amount of chromium picked up by abraded mild steel after three days immersion as a function of chromate concentration follows the form of a typical adsorption isotherm. They find a maximum of 5.5×10^{15} chromium atoms per cm^2 geometric surface. Considering a probable value of the roughness factor for an abraded surface equal to 3[22], and a diameter of CrO_4^{--} equal to

[22] T. L. O'Connor, Corrosion Lab., M.I.T., unpublished measurements.

$5.4 \overset{\circ}{A}$[23], their value corresponds to the equivalent of 4.5 layers of close-packed

[23] B. E. Warren, Private communication.

chromate ions. The number of layers would be less if correction were made for any chromate adsorbed on the air-formed surface oxide or reduced to chromic oxide during the three days exposure.

Powers and Hackerman[24], also using abraded steel, found in agreement

[24] R. Powers and N. Hackerman, J. Electrochem. Soc., 100, 314 (1953).

with Brasher and Stove that after two days immersion in 10^{-3} M radio-chromate at pH 7.5 there were 5.2×10^{15} chromium atoms remaining per cm^2 of surface, uniformly distributed.

Potential measurements of iron exposed to chromate solutions add to the
pertinent evidence concerning the mechanism of passivation. Data of this
kind are presented herewith, together with parallel data for 18-8 stainless
steel and titanium in other passivating electrolytes.

PROCEDURE

Potentials were measured using a precision potentiometer and vacuum-
tube galvanometer in conjunction with a silver chloride reference electrode
in 0.1 N KCl. The potential of the latter on the hydrogen scale omitting
liquid junction potentials is 0.288 volt at 25°C. All measurements were.
conducted in an air thermostat maintained within 0.2°C of 25°C. Final values
are for steady state where the net change within 12 hours was less than 5
millivolts. This often required successive measurements over several days.
The maximum change, however, within a few centivolts was obtained usually
during the first 24 hours.

Iron electrodes were prepared from high-purity 0.030-inch diameter wire
obtained by courtesy of the National Bureau of Standards (C $<$ 0.001%, total
impurities about 0.008%). Six-inch lengths were mounted in glass tubing and
sealed using polystyrene cement with about 1 cm of wire projecting. The
surface was prepared by pickling in 10% H_2SO_4, followed by washing and
immediate transfer to the test solution.

Electrodes of 18-8 were prepared from Type 304 0.028-inch diameter wire.
The wire was first annealed by heating electrically to 1000°C and quenching in air,

then was pickled in 15 vol. % HNO_3, 2 vol. % HF at 70-80°C and washed. It was immersed directly into the electrolyte to a depth of about 1 cm.

Titanium electrodes were made by cutting thin strips of Bureau of Mines cold rolled titanium, followed by pickling in HNO_3-HF at 70-80°C. No heat treatment was employed.

Ferric ion concentration in sulfuric acid was determined by reduction first with stannous chloride, the excess of which was eliminated by adding $HgCl_2$, followed by titration with permanganate. Cupric ion concentration was determined by titration using thiocyanate. Dichromate or chromate solutions were made up by weighing out the required amount of salt. Low carbonate NaOH was prepared by cooling hot saturated NaOH and decanting into wax-lined bottles.

The cell used for potential determinations consisted of a 4-ounce bottle fitted with a rubber stopper. A salt bridge containing the same solution as the electrolyte made contact with 0.1 $\underline{N}$ KCl in which the silver chloride electrode was immersed. The latter electrode was mounted in a glass tube, the bottom of which was constricted to provide a liquid junction by means of a sealed-in asbestos fiber.

Air, first bubbled through caustic soda and water, was used to aerate and stir most of the solutions. When nitrogen was used, it was purified by passing over 4 feet of copper turnings maintained at 400°C.

In tests for reversibility, the same metal electrode was used throughout, but for measurements of potentials as a function of concentration, different electrodes in separate cells were set up. In view of the considerable time to reach steady state, the latter arrangement was the only practical procedure. This produced a greater scatter of the data but also made the observed correlation of potential with concentration more convincing.

IRON IN CHROMATES

Iron in contact with distilled water attains noble values of potential as K_2CrO_4 is added. At a concentration of 0.0025 molar, the potential change is about 0.5 volt (Fig. 1). Further change at higher concentrations is not pronounced. The maximum potential change agrees with data presented by Burns[25]

[25] R. M. Burns, J. Applied Phys., 8, 398 (1937).

for iron in 0.01 N $K_2Cr_2O_7$ solution.

On first immersing the electrodes in a dilute solution of chromate, potentials are relatively active, changing to more noble values within about 2 to 4 hours. The time required is less as the concentration of chromate increases. Steady-state values in all cases were reached in less than 24 hours.

When the electrodes at steady state in 0.0025 M chromate are transferred to progressively more dilute solutions, it is found that a maximum of half the ennobling effect of the chromate is lost. This is true even after exposure to distilled water for 41 hours.

18-8 STAINLESS STEEL AND TITANIUM

18-8 stainless steel corrodes in dilute sulfuric acid, but corrosion is effectively inhibited[26] on addition of small amounts of ferric or cupric salts.

[26] "Stainless Iron and Steel", J. Monypenny, 3rd ed., p. 302, Chapman and Hall, London, 1951.

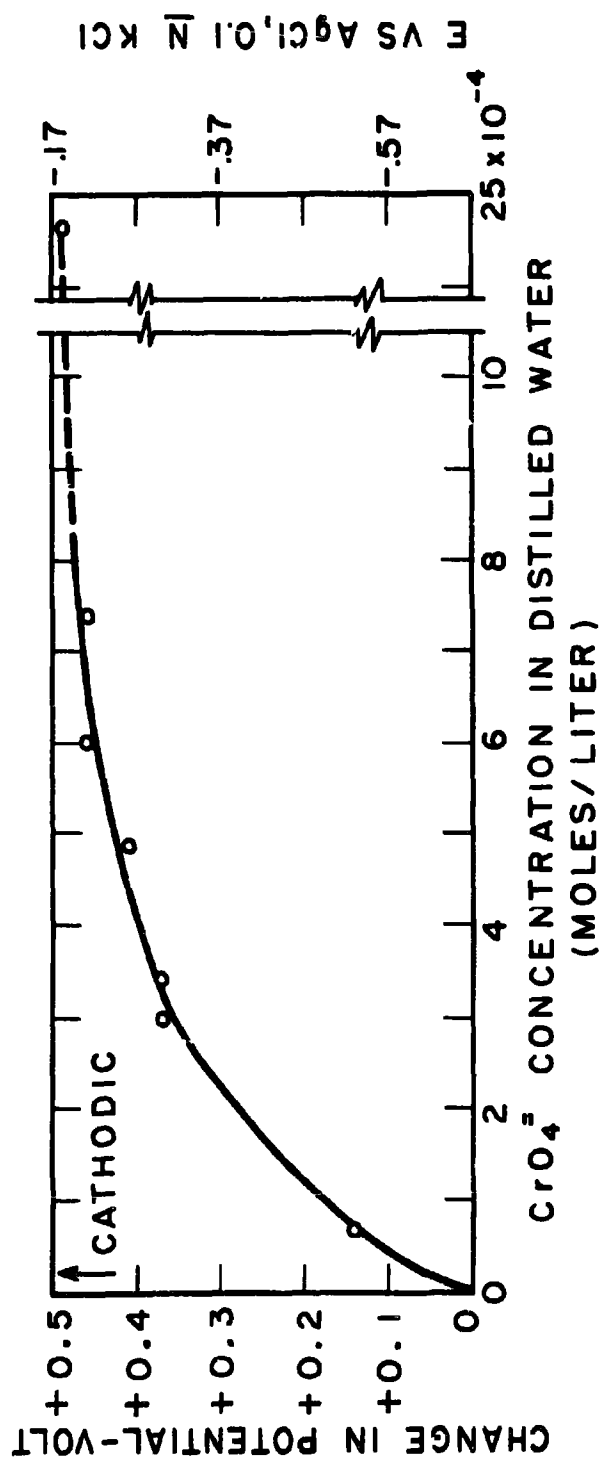Figure 1   Effect of $CrO_4^=$ Additions on the Electrode Potential of Electrolytic Iron in Distilled Water.   T = 25.0 ± 0.2°C. Aerated Solutions.

Similar inhibition is observed to hold for titanium[27,28], but with the dif-

[27] J. Cobb and H. H. Uhlig, J. Electrochem. Soc., 99, 13 (1952).

[28] D. Schlain and J. Smatko, J. Electrochem. Soc., 99, 417 (1952).

ference that the beneficial effects extend to hydrochloric acid, unlike the

situation for 18-8. It is of interest, therefore, to determine the parallel

potential behavior of 18-8 and titanium in sulfuric acid as these inhibitors

are added. The potentials in 0.2 N H_2SO_4 containing up to 0.191 M ferric sulfate

are summarized in Fig. 2, and for similar additions of cupric sulfate up to 0.70

M in Fig. 3. The potentials of 18-8 in ferric sulfate solution, followed for

several days, are found to become more noble by a maximum of 0.32 volt, whereas

titanium similarly is ennobled to a maximum of 0.39 volt. Since 18-8 is initially

more noble than titanium by 0.13 volt, the final potentials are not far different.

The general reproducibility of the measurements can be gaged by a comparison

of two separate runs for 18-8 in aerated solutions. In addition, one run in

nitrogen-saturated solution showed that oxygen exerts no effect on the

potential behavior.

Potentials of 18-8 and titanium are not reversible as shown by data of

Table I. On immersing 18-8, previously at steady state in 0.19 M Fe^{+++}, into

0.002 M Fe^{+++} (referring to 0.2 N H_2SO_4), the second steady-state potential

remained more noble by 0.07 volt after 27 hours exposure than the original

steady state value of 0.18 volt. However, on re-immersing the electrode into

0.19 M Fe^{+++}, the potential of 0.35 volt at the end of 20 hours was only 0.04
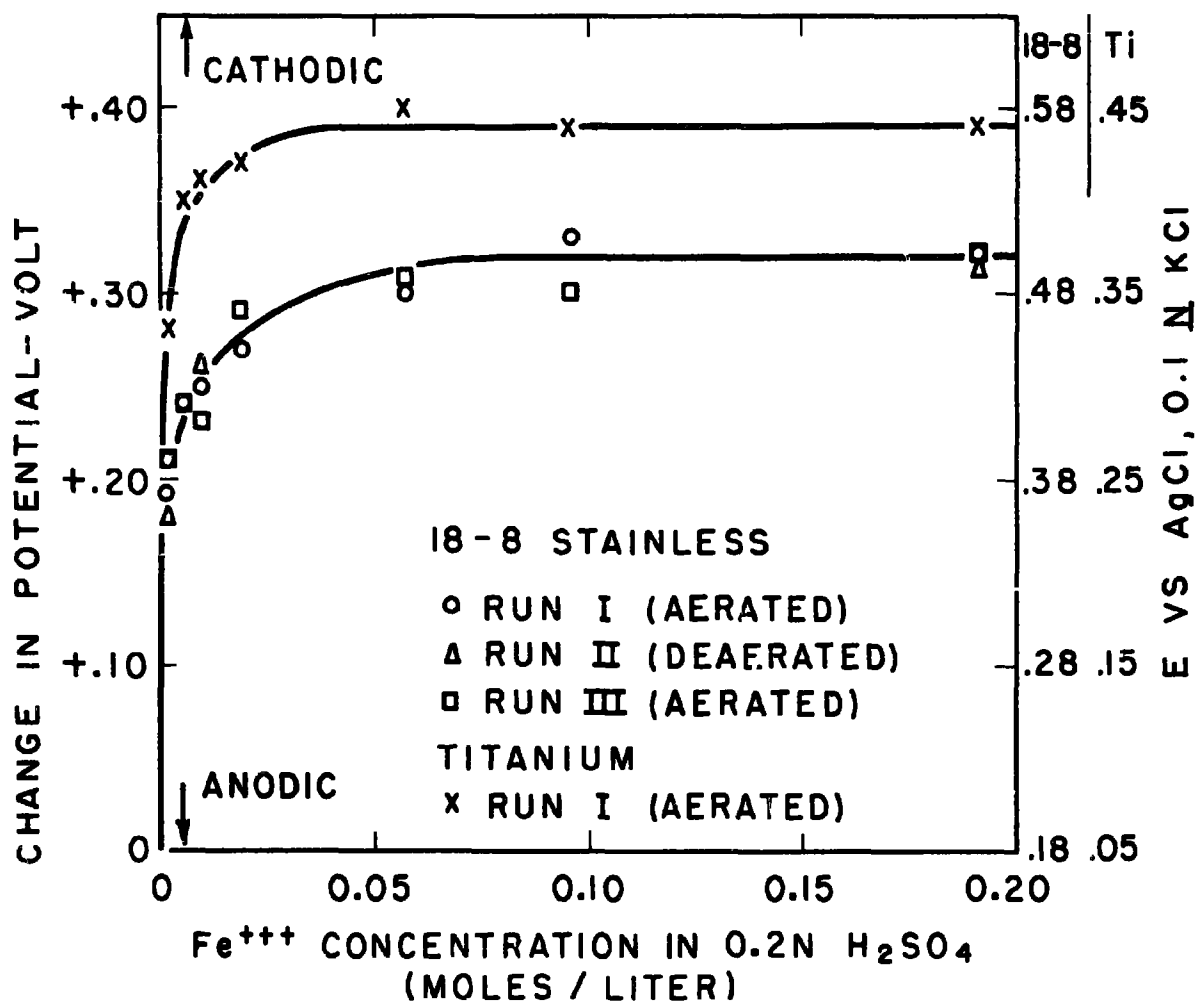
volt more noble than the original value.

Figure 2   Effect of Fe^{+++} Additions on the Electrode
Potentials of 18-8 Stainless Steel and Titanium
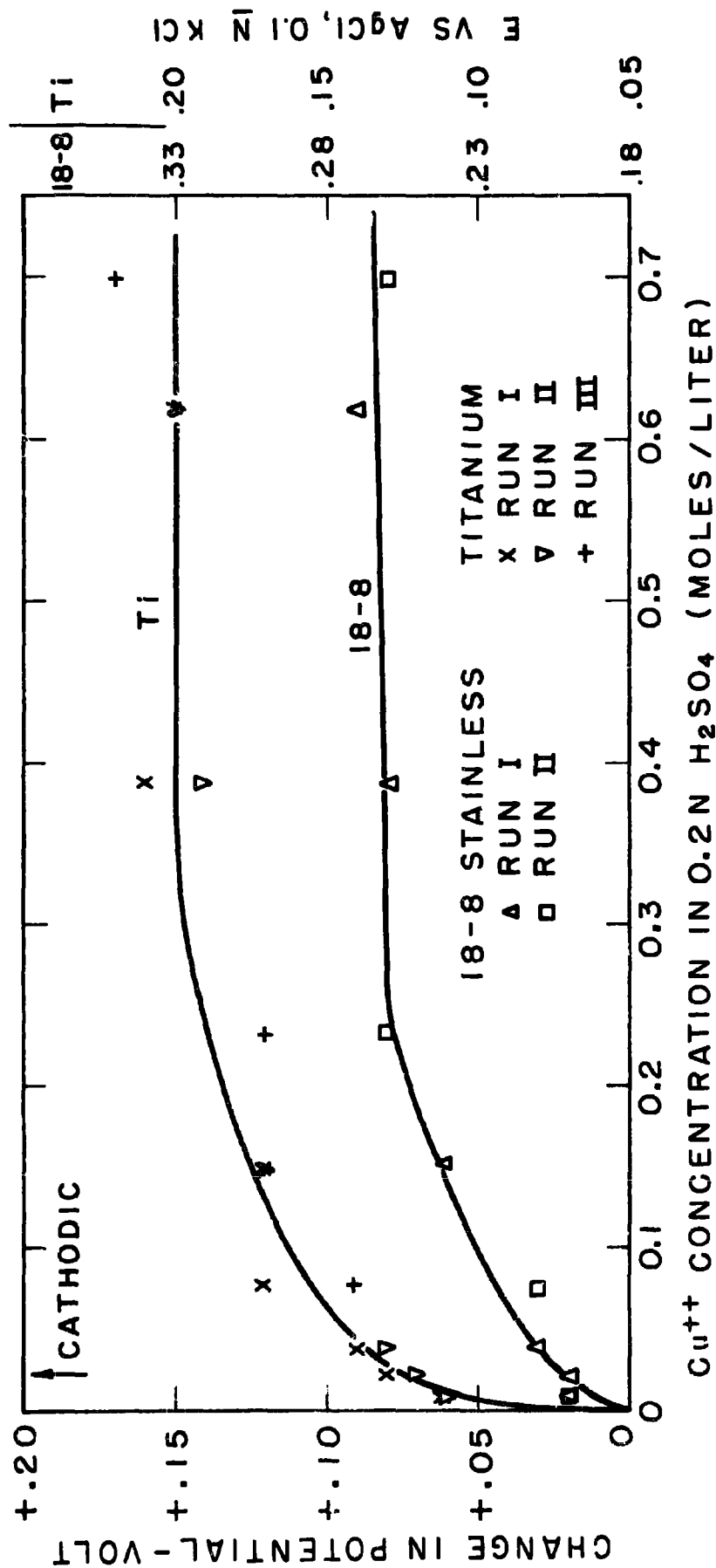in 0.2 $\underline{N}$ H$_2$SO$_4$. T = 25.0 ± 0.2°C.

Figure 3   Effect of Cu^{++} on the Electrode Potentials of 18-8 Stainless Steel and Titanium in 0.2 $\underline{N}$ H_2SO_4.

T = 25.0 ± 0.2°C.   Aerated Solutions.

TABLE I

TEST OF REVERSIBILITY

18-8

Electrolyte	Initial ΔE (volt)	Change of Concentration in moles/liter	Final ΔE (volt)
0.19 $\underline{M}$ Fe^{+++} in 0.2 $\underline{N}$ H$_2$SO$_4$	0.31		
	0.26	Decrease to 0.010	.27 (4 hrs)
	0.18	" " 0.002	.25 (27 hrs)
	0.31	Increase to 0.191	.35 (20 hrs)

Titanium

Electrolyte	Initial ΔE (volt)	Change of Concentration in moles/liter	Final ΔE (volt)
0.70 M Cu^{++} in 0.2 $\underline{N}$ H$_2$SO$_4$	0.17		
	0.12	Decrease to 0.23	.16 (1 hr)
	0.09	" " 0.078	.14 "
	0.00	" " 0.0	.12 "
	0.09	Increase to 0.078	.13 "
	0.12	" " 0.23	.17 "
	0.17	" " 0.70	.19 "

Iron

Electrolyte	Initial ΔE (volt)	Change of Concentration in moles/liter	Final ΔE (volt)
2.5 × 10^{-3} $\underline{M}$ K$_2$CrO$_4$	0.49 volt	Decrease to 0.0	.25 (41 hrs)
0.35 $\underline{M}$ NaOH in 4% NaCl	0.45		
	0.18	Decrease to 0.04	.20 (1 hr)
	0.15	" " 0.025	.17 "
	0.00	" " 0.0	.10 "
	0.15	Increase to 0.025	.17 "
	0.18	" " 0.04	.18 "
	0.45	" " 0.35	.35 "

With cupric sulfate additions, the potential changes are less than for ferric sulfate, even though the final concentration of cupric ion is higher. Maximum ΔE averaged 0.08 volt for 18-8 and 0.15 volt for titanium.

In aerated NaCl, 18-8 stainless steels in time corrode by pitting. Addition of alkali inhibits this type of attack[29]. Titanium, on the other

[29]H. H. Uhlig and J. W. Matthews, Corrosion, 7, 419 (1951).

hand, is relatively resistant to pitting in chloride solutions without alkali additions, including sea water. The potential behavior of 18-8 in 4% NaCl upon addition of NaOH up to 2.9 molar are shown in Fig. 4, and similarly in Fig. 5 for titanium with addition of NaOH up to 0.2 molar. Potentials were followed for a total period of about 120 hours. The remarkable difference in behavior of the metals in this electrolyte compared with previous electrolytes is that NaOH additions produce more _active_ potentials, or decrease passivity as measured by potential. The effects are most pronounced with first additions of NaOH below about 0.01 molar, subsequent additions producing only slight change. The maximum change of potential for 18-8 was -0.33 volt and for titanium -0.38 volt, indicating again similar behavior of both metals.

It was also of interest to learn the effect of oxygen on the potentials of 18-8 in this system, because of the importance oxygen has with respect to passivity of stainless steels exposed to the atmosphere. Potential measurements were carried out in 4% NaCl containing 0.3 $\underline{M}$ NaOH through which nitrogen, oxygen or air was bubbled. Also, one gas mixture was prepared, containing 0.05 atm. partial pressure oxygen, by compressing air and nitrogen to appropriate

pressures in a single gas cylinder and using this mixture to aerate and stir the electrolyte. The results are given in Fig. 6 showing that oxygen, as expected, ennobles the potential of 18-8 as the partial pressure increases.

Out of curiosity, potentials were also determined for iron in 4% NaCl as a function of NaOH additions. Here the potential becomes more noble, opposite to the trend for 18-8 or titanium (Fig. 7). About 24 hours or less were required for steady state. The values, on immersing the electrodes in several more dilute NaOH solutions after reaching steady state in 0.35 $\underline{M}$ NaOH, were the same as previously determined within 0.02 volt (after one hour) and on returning the electrode to 0.35 $\underline{M}$ NaOH, the potential was less noble by 0.1 volt (Table I). It is especially significant that the potential of iron, initially active in 4% NaCl, and the potential of 18-8 initially noble, approach the same value on additions of NaOH. The initial potential of iron vs Ag-AgCl, 0.1 $\underline{N}$ KCl is 0.78 volt which becomes more noble on OH$^-$ additions by 0.46 volt making the final potential 0.32 volt active to Ag-AgCl. The potential of 18-8, on the other hand, is initially 0.05 volt noble to Ag-AgCl becoming more active by 0.33 volt or finally 0.28 volt active to Ag-AgCl, a value which is nearly the same as 0.32 volt for iron. This suggests that the final surface states of iron and 18-8 (which contains 74% iron) in alkaline NaCl are comparable, despite large initial differences in neutral NaCl. Accordingly, it is not surprising that the corrosion rates in alkaline NaCl are comparably low for both metals, but are quite different in neutral or near neutral NaCl solutions.
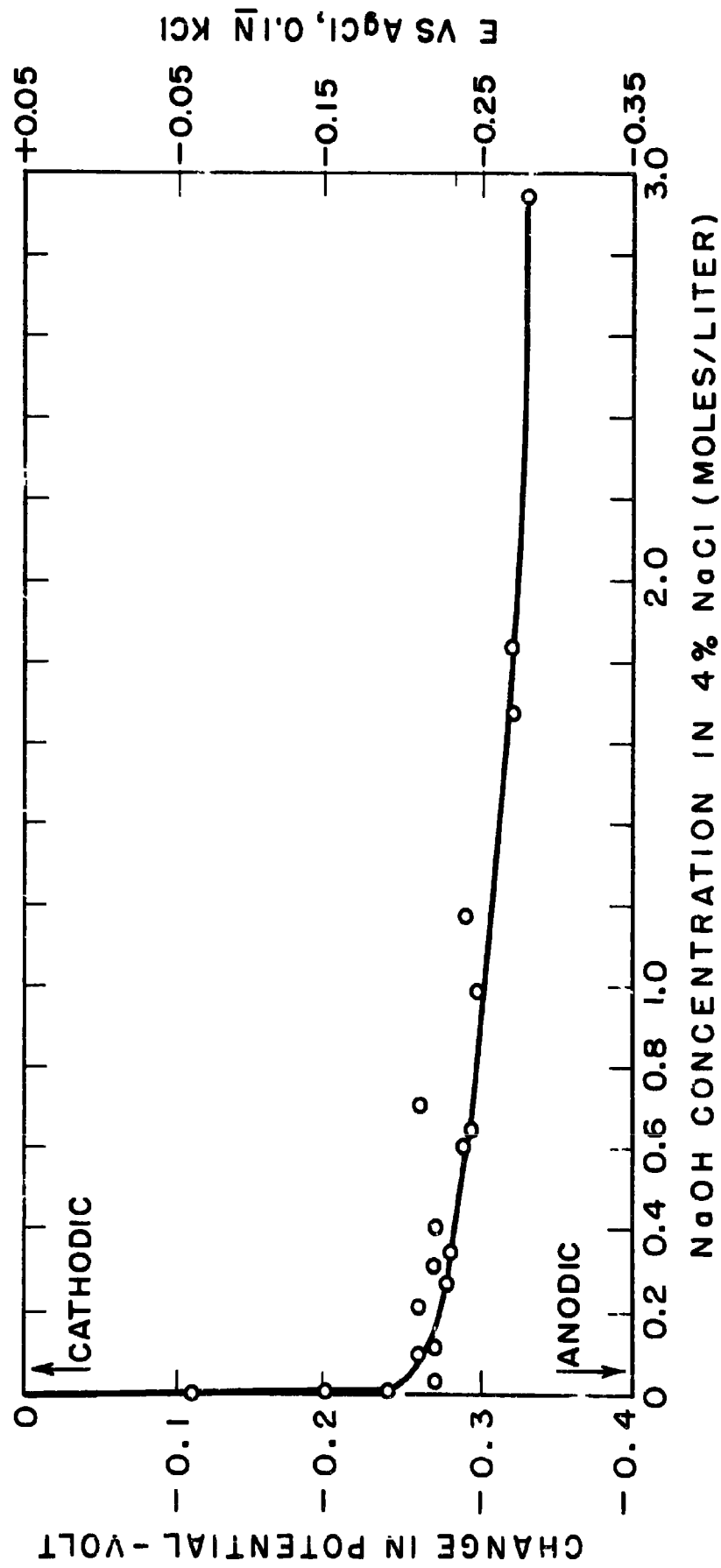
- 13 -

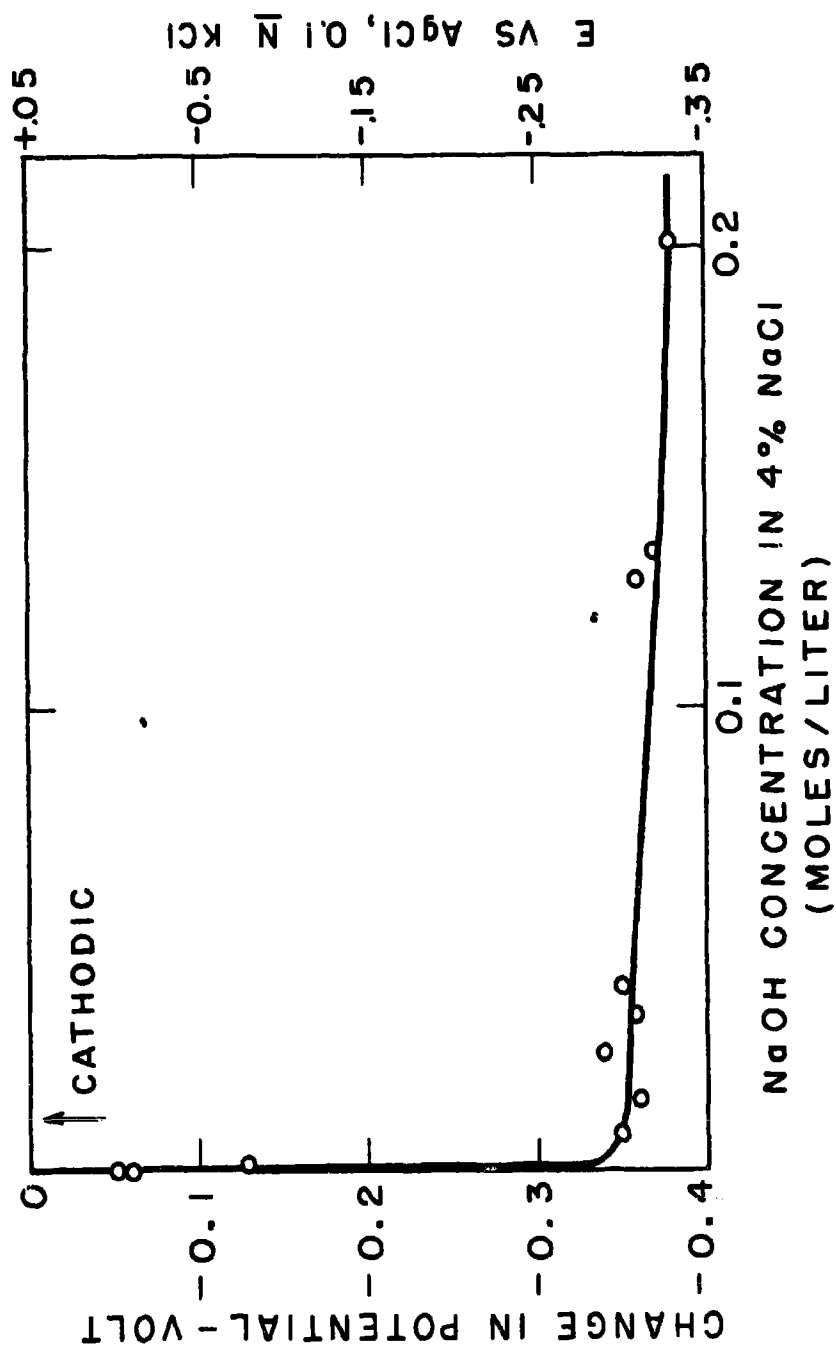Figure 4 Effect of NaOH Additions on the Electrode Potential of 18-8 Stainless Steel in Aerated 4% NaCl. T = 25.0 ± 0.2°C.

Figure 5 Effect of NaOH Additions on the Electrode Potential of Titanium in Aerated 4% NaCl. T = 25.0 ± 0.2°C.
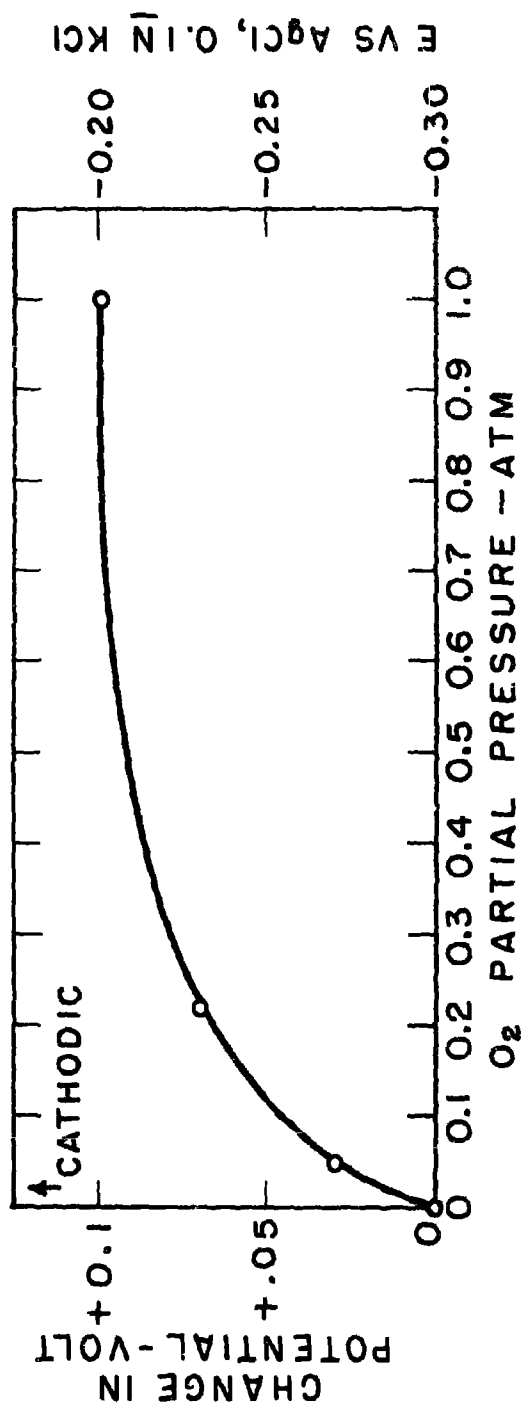
Figure 6   Effect of Varying O_2 Partial Pressure on the Electrode Potential of 18-8 Stainless Steel in 4% NaCl.   0.3 $\underline{M}$ NaOH.   T = 25.0 $\pm$ 0.2°C.
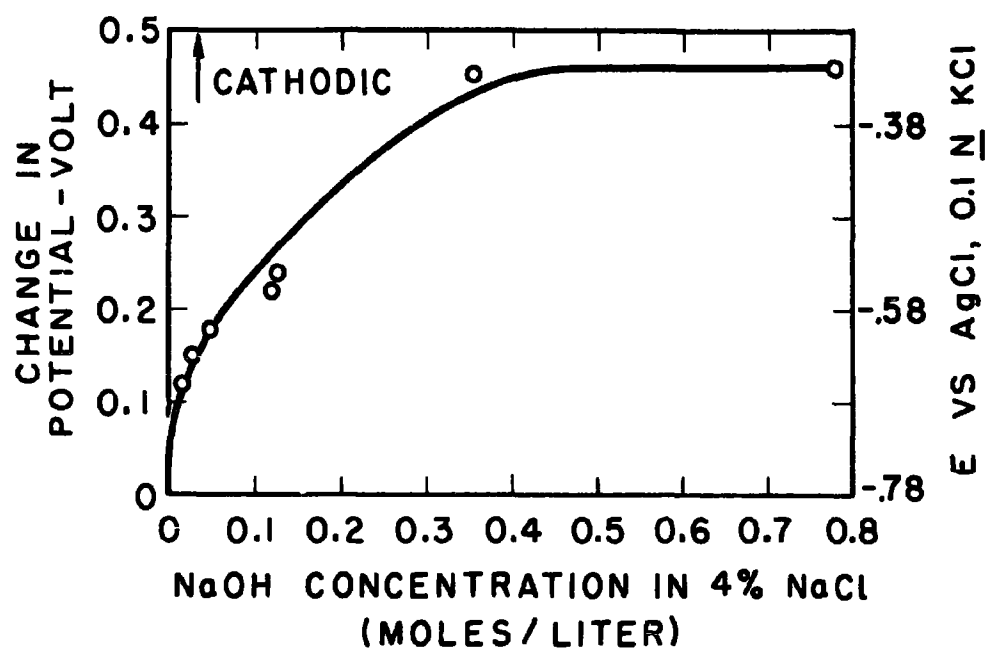
Figure 7   Effect of NaOH Additions on the Electrode
            Potential of Electrolytic Iron in 4% NaCl.
            T = 25.0 ± 0.2°C.   Aerated Solutions.

DISCUSSION

For each metal studied, the potential behavior as a function of passivator or inhibitor concentration resembles a typical adsorption isotherm. This relation is expected if inhibitors function by adsorbing on the metal surface, but would not be predicted, presumably, by any mechanism involving diffusion-barrier oxide or other type reaction-product films. Further consideration, therefore, of the data in light of adsorption appears worthwhile.

THE ADSORPTION ISOTHERM AND POTENTIALS

The adsorption isotherm proposed by Langmuir[30] is expressed as follows:

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[30] I. Langmuir, J.A.C.S., 40, 1361 (1918).

$$x = \frac{abp}{1 + ap}$$

where x is the amount of gas adsorbed per unit area at pressure p, and a and b are constants. The constant $\underline{b}$ is equal to maximum adsorbate x_m at high values of $\underline{p}$, and $\underline{a}$ is related to heat of adsorption[31]. Assuming that Henry's

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[31] I. Langmuir, J.A.C.S., 54, 2798 (1932).

Law applies, this can be converted to a similar expression for adsorption from liquids where concentration of solute C substitutes for gas pressure p.

Furthermore, if the ions adsorbing on a metal surface form dipoles each of electric moment P, electrostatic theory leads to the expression $4 \pi n P$

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for the total change of potential ΔE produced by $\underline{n}$ dipoles adsorbing per unit area of metal surface[*]. Therefore, ΔE is proportional to x, and maximum ΔE_m is similarly proportional to x_m.

Therefore, $$\frac{C}{\Delta E} = \frac{C}{\Delta E_m} + \frac{1}{a'\Delta E_m}$$

If the Langmuir isotherm applies, therefore, a linear relation should exist between $\frac{C}{\Delta E}$ plotted with C, the slope of which is equal to $\frac{1}{\Delta E_m}$, and the intercept is equal to $\frac{1}{a'\Delta E_m}$ at C = 0. The data for various inhibitor concentrations satisfactorily conform to this relation as shown by Figs. 8 to 13. Potentials for 18-8 and titanium in 0.2 $\underline{N}$ H_2SO_4 containing Cu^{++} show a degree of scattering, caused probably by the small measured potential differences in these solutions compared with experimental variations, the maximum ΔE being only 0.08 to 0.15 volt. $\frac{C}{\Delta E}$ versus C was not reproduced for Ti and 18-8 in 4% NaCl + NaOH, even though linearity is obtained for all but the lowest NaOH concentrations. The test of linearity, however, loses significance when values of ΔE are essentially constant with change of inhibitor concentration, as is true in this instance.

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[*]If one considers a supplementary diffuse double layer in accord with Gouy and Chapman, the additional potential change equals $\frac{4\pi\sigma}{D\mathcal{H}}$ [32] where σ is the

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[32] "Introduction to Electrochemistry", S. Glasstone, p. 524, D. Van Nostrand (1942).

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total electric charge per unit area, D is the dielectric constant, and $\mathcal{H}$ is equal to $(\frac{4\pi e^2}{Dkt}\sum n_i z_i^2)^{\frac{1}{2}}$ having the same significance as in the Debye-Hückel theory of electrolytes. Since $\mathcal{H}$ has the dimensions of reciprocal length and may be identified with the effective separation of charges in the dipole layer, this expression, if D = 1, achieves the same form as the expression for a fixed dipole layer.
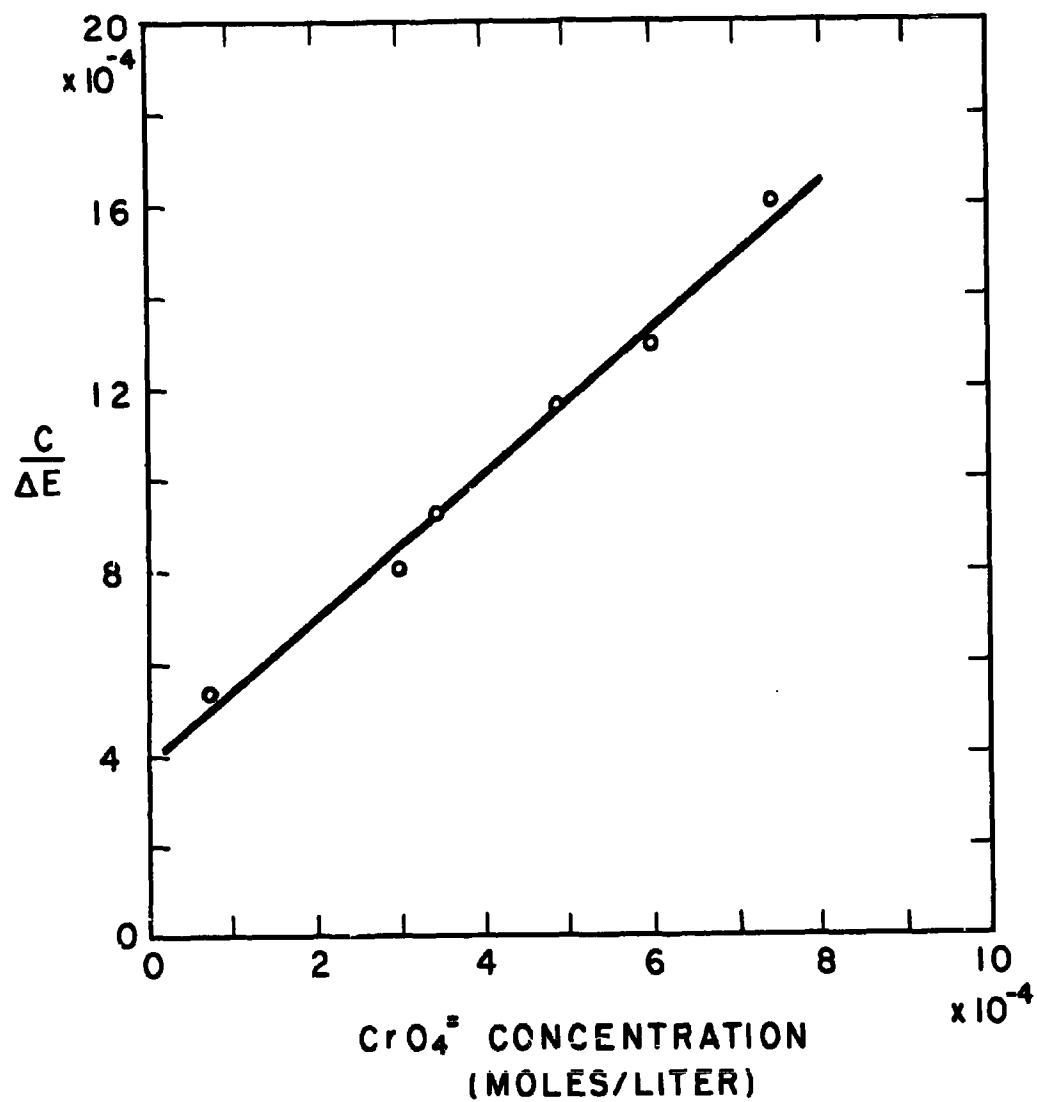
Figure 8   Langmuir Adsorption Plot for Electrolytic Iron
            in Distilled Water Containing $CrO_4^=$ Inhibitor.
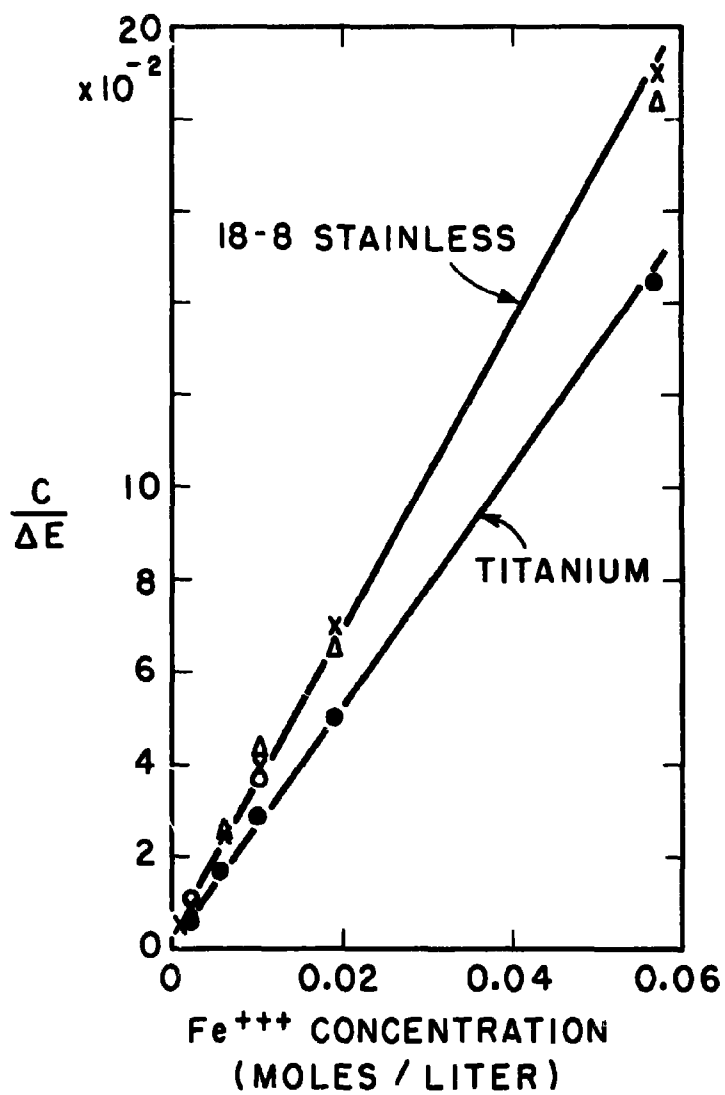   T = 25.0 ± 0.2°C.

Figure 9   Langmuir Adsorption Plot for
18-8 Stainless Steel and
Titanium in 0.2 $\underline{N}$ H_2SO_4
Containing Fe^{+++} Inhibitor.
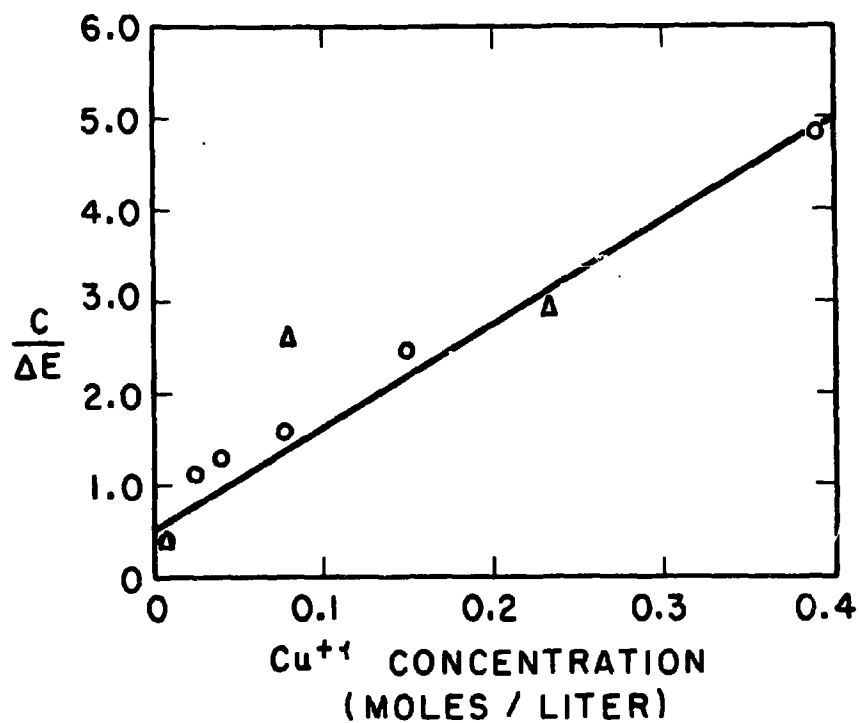T = 25.0 ± 0.2°C.

Figure 10   Langmuir Adsorption Plot for 18-8
             Stainless Steel in 0.2 $\underline{N}$ H_2SO_4
             Containing Cu^{++} Inhibitor.
             T = 25.0 ± 0.2°C
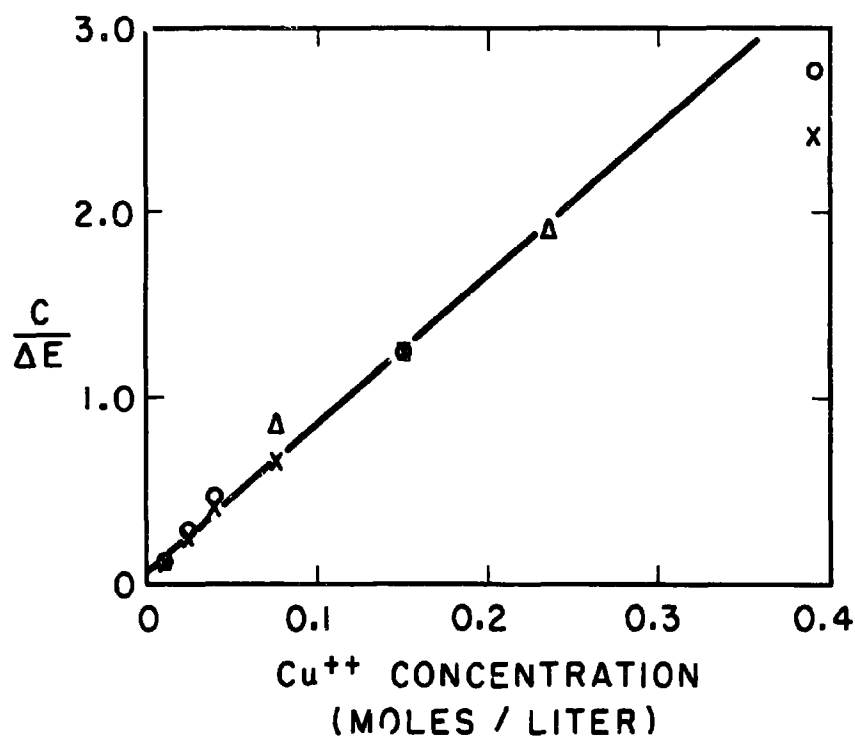
Figure 11   Langmuir Adsorption Plot for Titanium
in 0.2 $\underline{N}$ H$_2$SO$_4$ Containing Cu^{++} Inhibitor.
T = 25.0 ± 0.2°C.

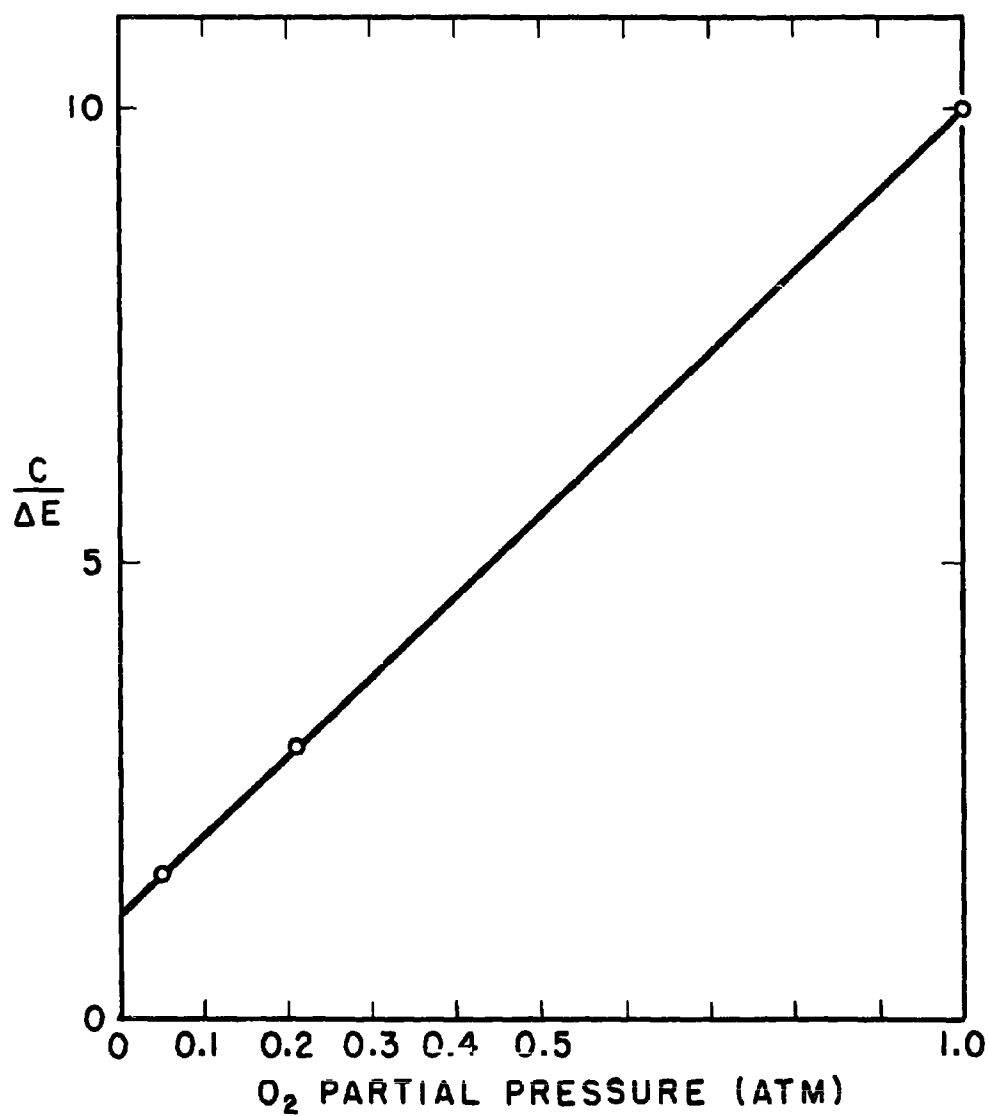Figure 12 Langmuir Adsorption Plot for 18-8 Stainless
Steel in 4% NaCl with 0.3 $\underline{M}$ NaOH, Varying O_2
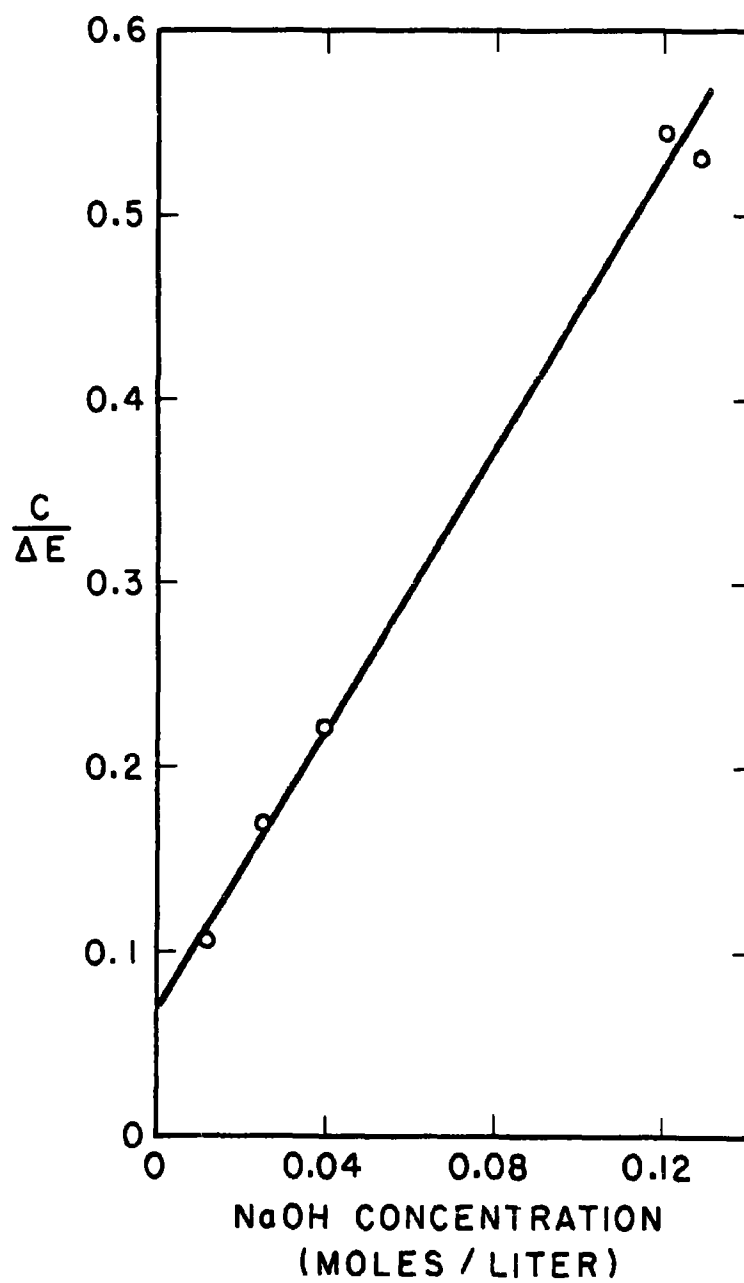Partial Pressure. T = 25.0 $^+_-$ 0.2°C.

Figure 13   Langmuir Adsorption Plot for
Electrolytic Iron in Aerated 4%
NaCl with NaOH Additions.
$T = 25.0 \pm 0.2°C.$

Correspondence, by and large, of the potential data to the Langmuir type isotherm points strongly to the view that the presently considered inhibitors function by adsorbing on the metal surface. Furthermore, the observed correspondence suggests adsorption of the monolayer type, as was pointed out by Langmuir in the derivation of his isotherm equation. These conclusions are strengthened by measurements of Hackerman and Sudbury[33], showing that potentials

[33]N. Hackerman and J. Sudbury, J. Electrochem. Soc., 97, 109 (1950).

of steel in contact with organic amine inhibitors also follow the Langmuir adsorption isotherm. The linearity of $\frac{C}{\Delta E}$ versus C reported by them is especially significant, since it is generally conceded that organic inhibitors function by adsorbing on the metal surface[34,35].

[34]"Metallic Corrosion, Passivity and Protection", U. R. Evans, p. 537, Ed. Arnold and Co., London (1946).

[35]T. P. Hoar, Pittsburgh International Conference on Surface Reactions, p. 127, Corros. Pub. Co., Pittsburgh (1948).

Maximum potential change, in accord with present considerations, occurs with formation of a complete monolayer of chemisorbed ions, any additional adsorption being accompanied by relatively small potential changes and lesser effects on the corrosion rate. It is important to note, therefore, that maximum change of ΔE in Fig. 1 for iron in chromates occurring at 2.5×10^{-3} molar, corresponds approximately to the minimum concentration of chromates (1×10^{-3} molar) found necessary by Robertson[8] for inhibition and passivity. It is

probably reasonable to conclude, therefore, that optimum passivity is associated with a monolayer film of adsorbed chromate ions.

Part of the adsorbed chromate is chemisorbed and part is reversibly adsorbed, as is pointed out by the time necessary to achieve steady state potentials, indicative of the usually longer times required for chemisorption, and by the partially irreversible nature of the potentials. Even after thorough washing in distilled water, iron passivated in radioactive chromates shows residual radioactivity[19,21,24], and the potential is more noble than initially. The final irreversible or chemisorbed portion exerts about half the total effect on the potential. This result is in agreement with a similar observation of Gatos[36] who found that on first immersing iron in chromate solutions, the

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[36]H. C. Gatos and H. H. Uhlig, J. Electrochem. Soc., 99, 250 (1952).

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amount of metal reacting initially when iron is made passive in concentrated nitric acid is less than in absence of chromate exposure, and that half this effect of chromate, but no more, could be removed by preliminary washing in water.

Powers and Hackerman[24] suggested adsorption of chromate ions on a surface oxide rather than on the metal. Although such adsorption presumably may occur, any mechanism of corrosion protection accompanying a film of this kind is not yet clear. An air-formed film, at least, is not necessary to adsorption. Preliminary measurements in this laboratory using radio-chromate showed that the usual radioactivity is picked up by oxide-free Armco iron sheet (0.024% C). The iron specimens were heated in dried pure H_2 at 1000°C, cooled in this gas, transferred to deaerated 10^{-3} M $Cr^{51}O_4$, pH 1.9, out of contact with air, and after 2 to 17.5 hours, washed successively in three 200 ml portions

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of distilled water. Somewhat greater residual chromium (3×10^{16} atoms/cm^2) was found than that reported by Brasher and Stove and by Hackerman and Powers for abraded iron. No residual radioactivity was found on similar specimens immersed directly into deaerated radioactive chromic perchlorate of pH 1.9.

ADSORPTION OF OXYGEN AND FERRIC, CUPRIC AND HYDROXYL IONS

Presumably, ferric and cupric ions also adsorb on 18-8 and titanium, producing passivity as gaged by reduced corrosion rates or noble potentials. The ions have a certain electron affinity and when adsorbed receive a certain amount of negative charge from the metal. The net effect including the effect of negative ions in solution, is an overall negatively charged ion layer near the surface and an equal positive image charge in the metal, similar to the situation for chromates. This accounts for increasingly noble potentials as more ferric and cupric ions adsorb, trivalent ferric ion being more effective in this respect than divalent cupric ion, corresponding also to the order of inhibition in dilute sulfuric acid[27].

The more active potentials of titanium and 18-8 in sodium chloride solution on addition of sodium hydroxide can be interpreted as c .. ...tion between hydroxyl ion and oxygen for a place on the metal surface, the adsorbed hydroxyl ion producing a lower order dipole moment than adsorbed oxygen. Chemisorbed oxygen, according to one viewpoint, is primarily responsible for passivity[5,37,38]

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[37] Ref. 7, p. 24.

[38] H. H. Uhlig, J. Electrochem. Soc., 97, 215C (1950).

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in these metals. If the partial pressure of oxygen is increased, the potential becomes more noble (Fig. 6) in agreement with this view. The potential

change from 0 to 1 atmosphere oxygen amounts to only 0.1 volt, suggesting

that the fundamental passive layer of chemisorbed oxygen in alkaline NaCl is

only slightly disturbed by hydroxyl ions. This concurs with the observation

that apparent equilibrium in this instance is affected between dissolved gas

and molecularly adsorbed oxygen and not atomically adsorbed oxygen, as shown

by the linearity of $\frac{p}{\Delta E}$ plotted with $\underline{P}$ but lack of linearity plotting

$\frac{\sqrt{p}}{\Delta E}$ versus $\sqrt{p}$, where $\underline{p}$ refers to partial pressure of oxygen. Previous quanti-

tative adsorption data obtained for oxygen on 18-8[39] provided evidence, in

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[39] H. H. Uhlig and S. S. Lord, Jr., J. Electrochem. Soc., 100, 216 (1953).

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fact, that the alloy exposed two days to aerated water is covered by a close

packed atomic oxygen layer over which a molecular oxygen layer is adsorbed.

Were the chemisorbed atomic oxygen on 18-8 entirely displaced by OH⁻, the potential

change would be in the order of 0.5 volt, corresponding to complete breakdown

of passivity, but a potential change of 0.4 volt occurs only in concentrated

alkalies, e.g., 20% NaOH[40].

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[40] H. H. Uhlig, Trans. Am. Inst. Min. Met. Engrs., 140, 387 (1940).

When iron, on the other hand, is immersed in alkaline NaCl, the competi-

tion includes not only adsorbed OH⁻ and oxygen, but also adsorbed H. Iron

exposed to an aqueous solution has a definite tendency to react, liberating

hydrogen and hydrous ferrous oxide, the free energy for the reaction being

negative[41] and independent of pH, so long as these corrosion products form

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[41] J. C. Warner, Trans. Electrochem. Soc., 83, 319 (1943).

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and no other. Hydrogen so produced adsorbs on the iron surface and, in neutral or alkaline solutions, escapes reluctantly as H_2 impeding the corrosion reaction. With presence of dissolved oxygen, adsorbed hydrogen reacts to form water as rapidly as oxygen reaches the metal surface. If, however, rate of consumption falls below the diffusion rate to the surface, excess oxygen, in turn, can adsorb on the metal. This adsorption, when it occurs, is accompanied by a lowered corrosion rate and a more noble potential (passivity). Therefore, as hydroxyl ions are added to the solution, adsorbed H is increasingly displaced by OH^- and reaction of the former with dissolved oxygen slows down. Consequently, oxygen is in excess at the surface, and conditions are favored for its adsorption. Support of this state of affairs is provided by the observation that in absence of oxygen, the potential of iron in water is more active when alkalies[42,43] are added, as is expected on thermodynamic

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[42] A. Travers and J. Aubert, Comptes Rend., 194, 2308 (1932).

[43] E. Meunier and O. L. Bihet, Congres. Chem. Ind., p. 444 (1933).

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grounds[*]. Only in presence of oxygen does the potential become more noble, the measured potential being a compromise between the iron and oxygen electrode values. In acid media, on the other hand, the iron electrode covered with

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[*]The reduced solubility of the $Fe(OH)_2$ layer on the metal surface as pH increases serves to decrease activity of Fe^{++}. This accounts for a more active potential corresponding to the reaction $Fe \longrightarrow Fe^{++} + 2e$, the value for which in volts is $0.440 - 0.0295 \log S.P. + 0.059 \log I.C. + 0.059 \text{ pH}$ where S.P. is the solubility product of $Fe(OH)_2$ and I.C. is the ionization constant for water.

adsorbed hydrogen behaves approximately as a reversible hydrogen electrode[44,45].

[44] J. D'Ans and U. Breckheimer, Z. Elektrochem., 56, 585 (1952).

[45] "The Electrode Potential Behavior of Corroding Metals in Aqueous Solutions",

O. Gatty, and E. Spooner, p. 310, Oxford Press, 1938.

Since iron and 18-8 have about the same potential in aerated alkaline NaCl,

the inference is that if oxygen is chemisorbed on 18-8, it is also, under

these conditions, chemisorbed on iron and is responsible for observed passivity

in both metals. The energy of bonding of oxygen to the metal need not be the

same in both cases, however, and, therefore, the degree of passivity may

differ.

Powers and Hackerman showed that competitive adsorption of CrO_4^{--} and

OH^- takes place on $Cr^{(46)}$ and iron[24] surfaces, similar to competitive adsorp-

[46] N. Hackerman and R. Powers, J. Phys. Chem., 57, 139 (1953).

tion of H, O_2 and OH^- described above.

PITTING TENDENCIES OF 18-8 AND TITANIUM

Inhibition of pitting in 18-8 by hydroxyl ion can be accounted for by

the reduced difference of potential between active and passive areas in the

galvanic cells that account for pitting[47], since the passive areas are no

[47] Ref. 7, p. 165.

longer so noble as before. In addition, metal chlorides at incipient pits react with hydroxyl ions which migrate rapidly to anodic areas to form metal hydroxides. The hydroxides, unlike soluble chlorides, do not continuously destroy passivity or, what is the same, do not maintain activity at the site of chemical disturbance; hence, the pit never gets started. With titanium, the pitting tendency is decreased by the pronounced tendency of titanium chloride to hydrolyze to hydroxide or hydrous oxide even in absence of hydroxyl ions. Hence, titanium, better than 18-8, resists pitting in sea water, and the potential data indicate that in alkaline salt solutions, the tendency would be still less.

SEPARATION OF CHARGE IN THE DIPOLE LAYER

Values of ΔE in combination with the equation $\Delta E = 4\pi n \ell$ make it possible to calculate the average separation of negative charge in the adsorbed chromate layer from the iron surface. Assuming a diameter of chromate ion equal to 5.4 $\overset{o}{A}$, there will be 4.0×10^{14} ions per cm^2 adsorbed in a close packed monolayer. A layer based on true surface rather than apparent area would still be equivalent in projected dipole moment to this number of ions. Since the change of potential produced by a monolayer is 0.5 volt (Fig. 1), the calculated value of d where ℓ is equal to nde (n = number of ions per cm^2, d = separation of negative and positive charge, and e = electronic charge) is

$$\frac{0.5}{300 \times 4\pi \times 4 \times 10^{14} \times 4.8 \times 10^{-10}}$$ or 0.07×10^{-8} cm. Hence, the excess

electrons, according to this calculation, are, on the average, only 0.035×10^{-8} cm from the metal surface, since the positive image charge within the metal is at a similar distance from the surface. In other words, a relatively slight

assymetry of electron density at the metal surface suffices to explain the
observed adsorption potentials.

VALUES OF LANGMUIR CONSTANTS

Values of the Langmuir constants ΔE_m and a' are summarized in Table II.
In general, ΔE_m calculated from the slope of $\frac{C}{\Delta E}$ vs C agrees reasonably well
with the observed maximum ΔE_m. For iron in alkaline NaCl, the difference
in values suggests that the potential relations are more complex than the simple
adsorption of oxygen alone, in accord with the discussion of iron potentials
above.

Values of a', according to the Langmuir derivation, are larger as the
heat of adsorption increases. Hence, O_2 on 18-8 and chromates on iron show
appreciable affinity of adsorbate for metal. Similarly, ferric ions have
greater affinity for 18-8 and titanium than cupric ions. The low value of a'
for iron in alkaline NaCl supports the point of view that competitive chemi-
sorption takes place between several species, e.g., H, OH^- and O_2, heats of
adsorption for one species tending to cancel out heats of desorption for the
species it displaces. Competition between possible adsorbates very likely
accounts for the partial reversibility of potentials involving chemisorbed
films. In general, it should be emphasized that values of a' reflect a re-
sultant heat effect of one or more competitive adsorption processes, even if
the subsstance displaced is nothing more than physically adsorbed H_2O. The
primary process, of course, has the largest effect. By and large, relative
values of a' are in accord with the expected trend based on chemical properties
of the metals and adsorbates, and the observed potentials and corrosion behavior.

TABLE II

VALUES FOR CONSTANTS OF LANGMUIR ADSORPTION ISOTHERM

Electrode	Electrolyte	E vs AgCl, 0.0 N Inhib., Volt	ΔE_m (Volt) (calc)	ΔE_m (Volt) (obs)	Intercept $a'^{-1} \Delta E_m^{-1}$	a' (Liters/Mole)
18-8	Fe^{+++} in 0.2 $\underline{N}$ H_2SO_4	0.18	0.30	0.33	0.001	3300
	Cu^{++} " "	"	0.09	0.08	0.5	22
	O_2 in 0.3 $\underline{N}$ NaOH in 4% NaCl	-0.30	0.11	0.1	0.0011	8400
Ti	Fe^{+++} in 0.2 $\underline{N}$ H_2SO_4	0.05	0.37	0.38	0.001	2700
	Cu^{++} " "	"	0.13	0.15	0.15	50
Fe	OH^- in aerated 4% NaCl	-0.78	0.26	0.46	0.065	59
	CrO_4^{--} in H_2O	-0.67	0.63	0.5	0.00039	4000

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